

Synthesis and Characterization of Polystyrene-*b*-Poly(4-vinyl pyridine) Block Copolymers by Atom Transfer Radical Polymerization

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Abstract

We aimed at the synthesis of well-defined PS-*b*-P4VP by using atom transfer radical polymerization in two-step process. First, polystyrenes with benzyl bromide end group (PS-Br; by ATRP) were prepared as macroinitiator for the next ATRP of 4-vinyl pyridine and characterized these polymers from ¹H-NMR and MALDI-TOF. Comparing with MALDI-TOF-MS, ¹H-NMR and GPC analyses, this indicates that the formation of the block copolymer can be observed. During the polymerizations, molecular weight distribution and kinetics have been evaluated from GPC traces and ¹H-NMR analyses. We further characterized the thermal properties of these block polymers by DSC and TGA. DSC measurement on the PS-*b*-P4VP block copolymers exhibited two glass transitions, indicating that the resulting block copolymers are phase separated. Two maxima differential peaks were observed on the TGA trace for the PS-*b*-P4VP block copolymers might be assigned to the decomposition of the P4VP blocks at 380 °C and the PS blocks at higher temperature.

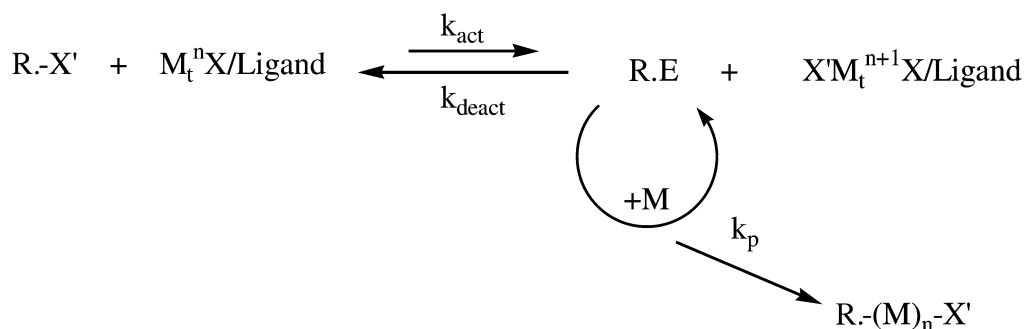
Introduction

The desire to control polymer properties through the synthesis of block copolymers and complex macromolecular architectures is a continuing theme throughout polymer chemistry [1, 2]. Block copolymers are remarkable self-assembling systems that can assume a wide variety of morphologies including lamellar, hexagonal-packed cylindrical, and body-centered cubic micellar structures, depending on the relative volume fractions of the blocks [3, 4]. This clear picture of the morphology as a function of composition has primarily emerged from the investigation of diblock copolymers. The block copolymers with well-defined structures, such as molecular weight (MW) and molecular weight distribution (MWD), composition, architecture and end group functionality, are very important, and this has been carried out by the following three methods [5]: (1) sequential monomer addition, (2) coupling reaction of “living” polymer chains, and (3) mechanism transformation. The development of ionic polymerization methods allowed for the preparation of well-defined polymers with controlled chain end functionalities and the synthesis of well-defined block and graft copolymers [6–9]. However, these polymerizations have to be carried out with nearly complete exclusion of moisture and air, and often at very low temperature. Moreover, only a few numbers of monomers can be polymerized, and the presence of functional monomers can cause undesired side reactions. Recently, Matyjaszewski has reported that atom transfer radical polymerization (ATRP) can be used to synthesize polymers with narrow molecular weight distribution (MWD) [10], well-defined block copolymers [11, 12], and

star polymers [13, 14]. The ATRP process uses an alkyl halide as initiator and a metal in its lower oxidation state with complexing ligands [15–21]. The process involves the successive transfer of the halide from the dormant polymer chain to the ligated metal complex, thus establishing a dynamic equilibrium between active and dormant species (Scheme 1). This controlled radical polymerization allows for the polymerization of a wide range of monomers such as styrenes [22, 23], acrylates [24, 25], methacrylates [26, 27], and various functional monomers.

It has been demonstrated that a block copolymer of P4VP has the ability to form self-assembly supramolecular structure [28], high complexibility with metal ion [29, 30], and electrical conducting property [31]. Polymerization of 4VP poses a very challenging problem for ATRP because both 4VP and P4VP are strong coordinating ligands that can compete for the binding the metal catalysts in these systems. Since the monomer is normally present in large excess over the employed ligand, there is a possibility of the formation of pyridine-coordinated metal ion complexes in the polymerization solution. Pyridine-coordinated copper complexes are not effective catalysts for ATRP. For example, addition of 5 vol% pyridine to the polymerization solution of styrene catalyzed by CuBr complexed by 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) significantly slowed down the polymerization rate [21].

In this paper, we aimed at the synthesis of well-defined PS-*b*-P4VP by using atom transfer radical polymerization in two-step process by using commercial available ligands. First, polystyrenes with benzyl bromide end group (PS-Br; by ATRP) is prepared as macroinitiator for the next ATRP



Scheme 1. Dynamic equilibrium that exists between the propagating and dormant species when a metal complex is used as the reversible halogen atom transfer reagent.

of the 4-vinyl pyridine and characterized these polymers by $^1\text{H-NMR}$ and MALDI-TOF. During the polymerizations, molecular weight distribution and kinetics have been evaluated by GPC traces and $^1\text{H-NMR}$ analyses. We further characterize the thermal properties of these block polymers by DSC and TGA.

Experimental

Materials

Styrene (S) and 4-vinylpyridine (4-VP) were distilled from calcium hydride before use. Copper(I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and then rinsed with absolute ethanol under a blanket of argon and dried under vacuum at 80°C for three days. All solvents were distilled prior to use. N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA), 2,2'-bipyridine (Bipy), 4,4'-dinonyl-2,2'-dipyridyl (dNBipy) were used as received. N,N' -dimethylformamide (DMF) and toluene were distilled from magnesium sulfate and sodium/benzophenone immediately before use. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Preparation of PS-Br Macroinitiator by the ATRP of Styrene

A typical polymerization is as follows: CuBr (0.1 mmol) was placed into a dry 25-mL round-bottom flask equipped with a stirring bar. Toluene (10 mL), styrene (30 mmol) and PMDETA (0.1 mmol) were added sequentially and the solution was stirred for 20 min to form the Cu complex. The initiator, 1-phenylethyl bromide, (0.1 mmol) was then added. This whole process was carried out in a nitrogen-filled dry box. The mixture was degassed with three freeze-thaw cycles. Polymerization was carried out at an appropriate temperature in an oil bath. The reaction mixture turned dark green immediately and became progressively more viscous. Upon completion of the reaction, the mixture was diluted five-fold with tetrahydrofuran (THF) and stirred with of Amberlite IR-120 (H form) cation-exchange resin (3–5 g) for 30–60 min to remove the catalyst. The mixture was then passed through a neutral alumina column and precipitated into ten-fold of methanol. The resulting polymers were filtered and dried overnight at 60°C under vacuum.

Preparation of PS-*b*-P4VP by the ATRP of 4-VP with PS-Br Macroinitiator

A typical procedure for the synthesis of PS-*b*-P4VP was as follows. Prior to the sequential polymerization, the PS-Br macroinitiator was dried overnight in a vacuum oven at 50°C . In a flame-dried, two-necked flask, CuX (0.1 mmol) was placed into a dry 25-mL round-bottom flask equipped with a stirring bar. 4-VP (20 mmol), DMF (4 M) and a desired amount of ligand were added sequentially and the solution was stirred for 20 min to form the Cu complex. The macroinitiator (0.1 mmol) was then added. This whole process was performed in a nitrogen-filled dry box. The mixture was degassed with three freeze-thaw cycles. An aliquot of the solution (ca. 0.1 mL) was removed and then polymerization was carried out at an appropriate temperature in an oil bath. The reaction mixture turned dark green immediately and became progressively more viscous. Periodically, aliquots (0.1 mL) were removed for analysis. Exotherms of $2\text{--}4^\circ\text{C}$ were typically observed, indicating that polymerization occurred. Upon completion of the reaction, the mixture was diluted five-fold with DMF and stirred with of Amberlite IR-120 (H form) cation-exchange resin (3–5 g) for 30–60 min to remove the catalyst. The mixture was then passed through an alumina column and precipitated into ten-fold of 10% H_2O /methanol. This purification protocol resulted in the loss of up to 5–10% of the polymer as a result of adsorption. The resulting polymers were redissolve in DMF and precipitated into ten-fold of ether. The resulting polymers were filtered and dried overnight at 60°C under vacuum. These procedures were repeated twice to obtain the pure block copolymer.

Characterization

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra was performed on a PerSeptive Biosystems Voyager DE-STR equipped with 2-m linear and 3-m reflector flight tubes and a 337-nm nitrogen laser (pulse width, 3 ns), along with a delayed extraction capability. All experiments were carried out at an accelerating potential of 20 kV in both linear and reflector modes. In general, mass spectra from 256 laser shots were accumulated summed to produce a final spectrum. Angiotensin I (human; $M_w = 1296.5$) (BACHEM) and insulin

(bovine pancreas 28.3; $M_w = 5733.50$) (Nacalai) were used as internal standards to calibrate the mass scale. Samples for MALDI-TOF-MS analysis were prepared by mixing the polymer, a matrix, and a cationizing agent in a solvent. For example, a PS sample (approximately 10 mg/mL) was dissolved in THF. The matrix [1,8-dihydroxy-9(10H)-anthracenone; dithranol] and the cationizing agent (sodium trifluoroacetate) were also dissolved separately in THF (30 and 10 mg/mL, respectively). A 30 μL portion of the PS solution, 90 μL of the matrix solution, and 30 μL of the cationizing agent were mixed in a glass vial. The weight ratio of polymer/matrix/cationizing agent was thus 1/9/1. Then 0.5 μL portions of the mixture were deposited onto 10–20 wells of the gold-coated sample plate and dried in air at room temperature. NMR spectra were recorded on a Bruker AM500 Spectrometer and were measured in DMSO- d_6 . Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a Waters 510 HPLC – equipped with a 410 Differential Refractometer Index (RI) and a UV detector in series, and three Ultrastaygel columns (100, 500, and 10³ Å) connected in series in order of increasing pore size – using DMF as an eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained using polystyrene standards. Thermal analysis was carried out on a DSC instrument from DuPont (model 910 DSC-9000 controller) with a scan rate of 20 °C/min and temperature range of 20–200 °C in nitrogen atmosphere. Approximately 5–10 mg sample was weighted and sealed in an aluminum pan. The samples were quickly cooled to room temperature from the first scan and then scanned between 30 and 280 °C at a scan rate of 20 °C/min. The glass transition temperature is taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated glass and liquid lines. FTIR spectroscopy measurements were made from a NaCl disk using a Nicolet Avatar 320 FT-IR Spectrometer, with 32 scans collected at a resolution of 1 cm^{-1} . A DMF solution containing the sample was cast onto a NaCl disk and dried under conditions similar to those used in the bulk preparation. The sample chamber was purged with nitrogen to maintain the film's dryness. Thermogravimetric analysis (TGA) experiments were performed by using a DuPont TGA-51 thermogravimetric instrument. The temperature was increased from 30 to 800 °C at a heating rate of 20 °C/min under nitrogen atmosphere. The degradation temperature was defined as the temperature at the maximum of the differential thermogravimetric curve.

Results and Discussion

The synthetic approach for the PS-*b*-P4VP block copolymers is depicted in Scheme 2. Initially, it was decided to grow a well-defined polystyrene chain from the phenylethyl bromide initiator and resulted chain end functionalized PS acted as a polymeric initiator for the next controlled polymerization of 4-vinylpyridine. Figure 1 shows MALDI-TOF-MS and GPC curves of PS macroinitiators obtained from the different polymerization time interval. It can be

observed that variation of the PS molecular weight based on the MALDI-TOF-MS spectrum matches well with that from the gel permeation chromatography (GPC). The signals of every series in MALDI-TOF-MS spectrum are separated by 104 Da, corresponding to the molecular weight of a styrene unit. As observed by both MALDI-TOF-MS and GPC, peak maxima of these spectra clearly shift to high molecular weight with increasing monomer conversion.

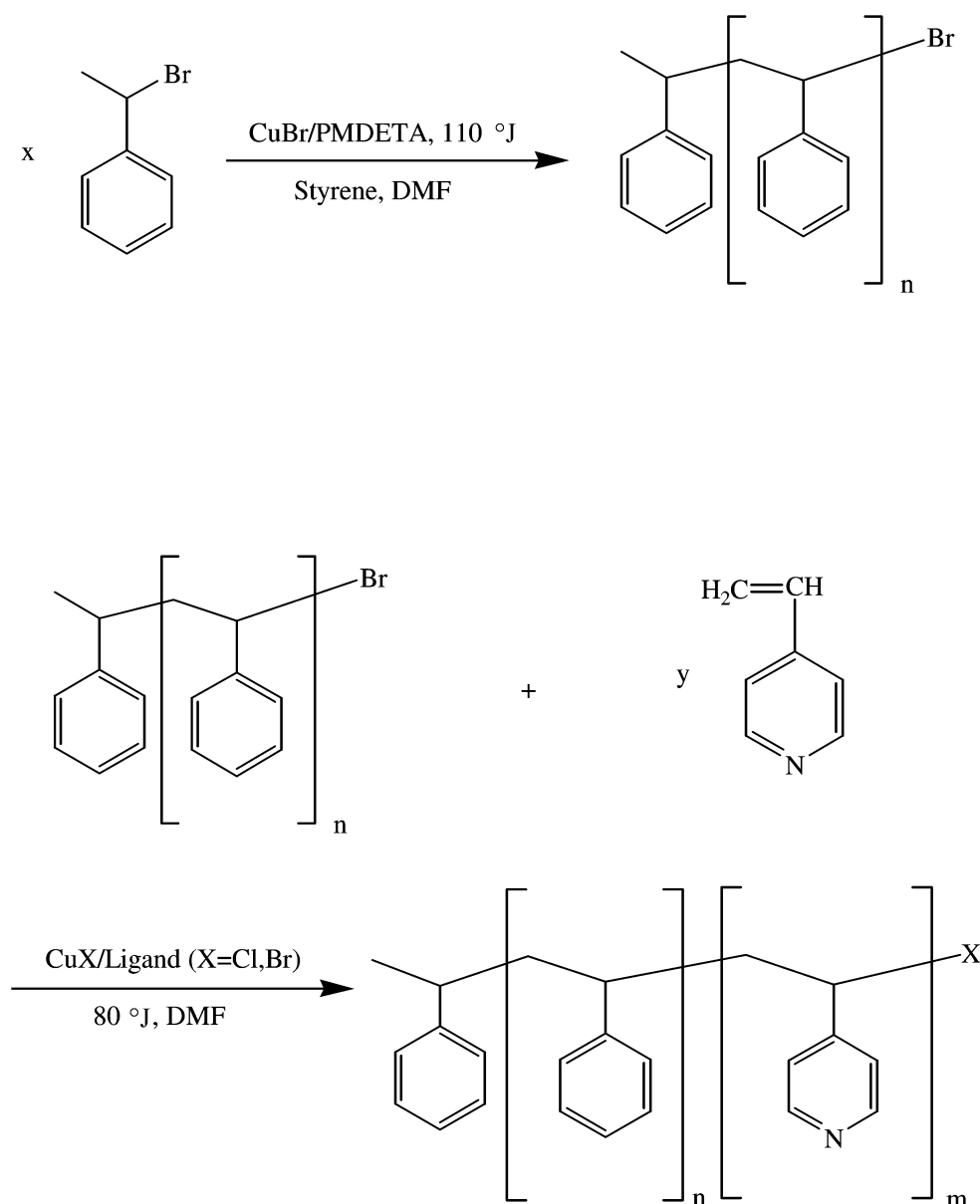
Sequentially, we use the PS-Br macroinitiator ($M_n = 8000$) to further polymerize with 4-vinylpyridine. The structure of the block copolymer was characterized by ¹H-NMR spectroscopy. Figure 2 illustrates the NMR spectra of PS-Br, PS-*b*-P4VP, and P4VP polymers. The spectrum of the block copolymer shows signal superposition of PS segments with attached segments of 4-vinyl pyridine. Comparing with MALDI-TOF-MS and GPC analyses, the formation of the PS-*b*-P4VP block copolymer can be identified.

In a typical ATRP, the concentration of the active species remains unchanged throughout the reaction that can be verified by a linear semilogarithmic plot of monomer conversion vs. time as shown in Figure 3 where conversion is calculated from ¹H-NMR of the feeding monomer initiated from PS-Br macroinitiator. If a stronger binding ligand was used, such as the tridentate PMDETA, a faster polymerization rate was observed. Under similar conditions, a PMDETA to CuBr ratio of 6 : 1 was needed to maintain a relatively fast polymerization rate to obtain a monomer conversion of 50% after 4 h. In contrast, at a PMDETA to CuBr ratio of 1 : 1, the polymerization was slower as shown in Figures 3(a) and 3(b). This result is quite similar with the earlier results on the polymerization of 4VP [31]. It is the evidence for the competitive coordination of 4VP monomer to copper. When polymerization of 4VP was carried out using macroinitiator and CuBr complexed by dNBipy as the catalyst in a ratio of 1 : 1 [Figure 3(d)], a very slow polymerization rate was observed. This is due to the same pyridine unit that functions as ligand and monomer, and hence, the dynamics equilibrium of the halogen atom transfer process will be disturbed. This undesired interaction will influence the polymerization rate and the molecular weight distribution during ATRP process. Even at a dNBipy to CuBr ratio of 6 : 1 as shown in Figure 3(c), it still showed a slower polymerization rate than that of PMDETA to CuBr ratio of 1 : 1. Various ligands, contents, reaction time, molecular masses (M_w), yield and PDI are summarized in Table 1. Overall, PMDETA system is the most efficient ligand for the polymerization of 4-vinylpyridine.

Figure 4 shows the dependence of the molecular weight of the block copolymers versus monomer conversion initiated by macroinitiator. The drawn line represents the theoretical molecular weight, $M_{n(\text{th})}$, calculated from:

$$M_{n(\text{th})} = \frac{\Delta[M]}{[I]_0} \times M_{w(\text{mon})} + M_{w(\text{init})}. \quad (1)$$

We observe a near-linear increase in the measured number average molecular weight (M_n) vs. monomer conversion up to ~75% and the evolution of molecular weight agrees with the theoretical value, indicating that a living/controlled polymerization process proceeds in solution.



Scheme 2. Reaction scheme for the syntheses of block copolymers.

The polymerization of 4-vinylpyridine initiated by PS macroinitiator was examined with and without halogen exchange. Figure 5 shows the kinetics plots of semilogarithmic of monomer conversion vs. time. The rate of polymerization without halogen exchange was faster than that with halogen exchange. The rate of polymerization in ATRP depends on the concentration of propagating radicals and is function of both the initiation efficiency and the concentration of deactivator in the system. For PS-Br/CuCl system, therefore, lower concentration of propagating radicals is obtained. The molecular weight also displayed a near-linear dependence on conversion (Figure 6). The molecular weight and polydispersity for the PS-b-P4VP block copolymers prepared with halogen exchange were lower than those without halogen exchange. The molecular weight distribution yielded by the PS-Br/CuX initiation system is worth to mention. The Cu(II)Br bond is relatively weaker than that of Cu(II)Cl, resulting in faster deactivation of the propagating radical and

lower polydispersity. This result is in accordance with the earlier results on the inhibition of radical polymerization of MMA by Cu(II)Br₂ and Cu(II)Cl₂ and trapping of alkyl radicals [33, 34]. Thus, for chain extension from PS to 4VP, introduction of halogen exchange technique should yield a more precisely controlled block copolymer than that without the halogen exchange.

Thermal behavior of block copolymers was examined by differential scanning calorimetry (DSC) in the range of 0 to 200 °C. The temperature at the midpoint of the baseline shift was defined as the bulk glass transition temperature, T_g . As shown in Figure 7, DSC measurement on the PS-b-P4VP block copolymers exhibited two glass transitions, indicating that the resulting block copolymers are phase separated. Typical T_g 's of PS, and P4VP are reported to be 100, and 150 °C. Obviously, the two glass transition temperatures are quite similar to those of respective homopolymers. This result indicates that the block copolymer is in a microphase-

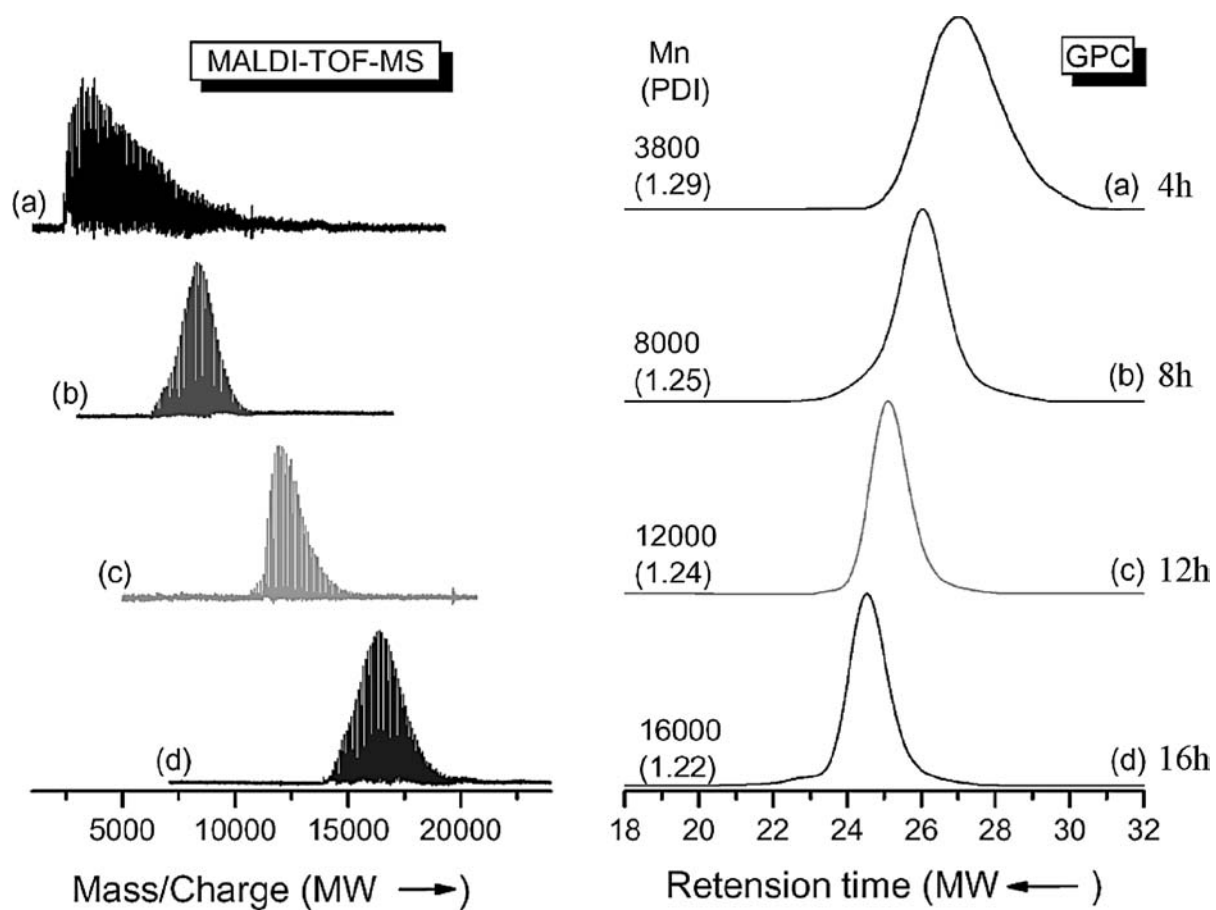


Figure 1. Comparing MALDI-TOF-MS and GPC of PS macroinitiators with the progress of polymerization: (a) 4h; (b) 8h; (c) 12h; (d) 16h.

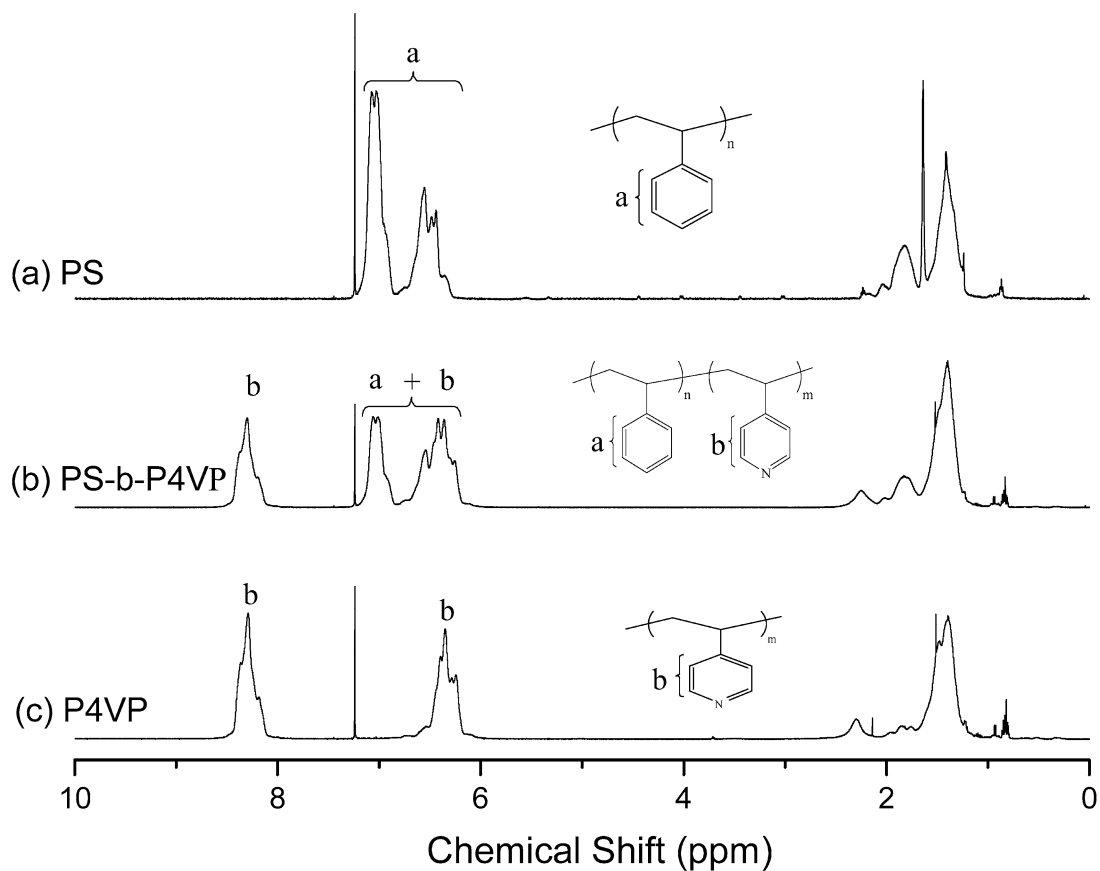


Figure 2. $^1\text{H-NMR}$ spectra of (a) PS, (b) PS-b-P4VP and (c) P4VP homo and block copolymer in $\text{DMSO-}d_6$.

Table 1. Block copolymerization conditions^a from PS^b to 4VP at 80 °C by ATRP

Sample	Ligand ^c	I : C : L ^d	Time (h)	Yield (%)	M_w (GPC) ^e	PDI
1	PMDETA	1 : 1 : 1	5	30	15300	1.33
2	PMDETA	1 : 1 : 1	9	48	18500	1.30
3	PMDETA	1 : 1 : 6	4	53	20300	1.32
4	PMDETA	1 : 1 : 6	9	74	23700	1.30
5	dNBipy	1 : 1 : 1	5	6	9400	1.43
6	dNBipy	1 : 1 : 1	9	11	10800	1.42
7	dNBipy	1 : 1 : 6	4	17	12000	1.43
8	dNBipy	1 : 1 : 6	9	48	17000	1.41
9	Bipy	1 : 1 : 6	24	8	10200	1.37

^a Monomer: 4vinylpyridine (4VP); solvent: *N,N'*-dimethylformamide (DMF); mole ratio of monomer/macro-initiator: 200 : 1.

^b PS macroinitiator: $M_n = 8000$, $M_w = 9600$, PDI = 1.20.

^c Ligand: PMDETA = *N,N,N',N'',N''*-pentamethyldiethylenetriamine; dNBipy = 4,4'-dinonyl-2,2'-dipyridyl; Bipy = 2,2'-bipyridine.

^d Mole ratio of initiator to copper bromide to ligand.

^e Polydispersity index from GPC traces.

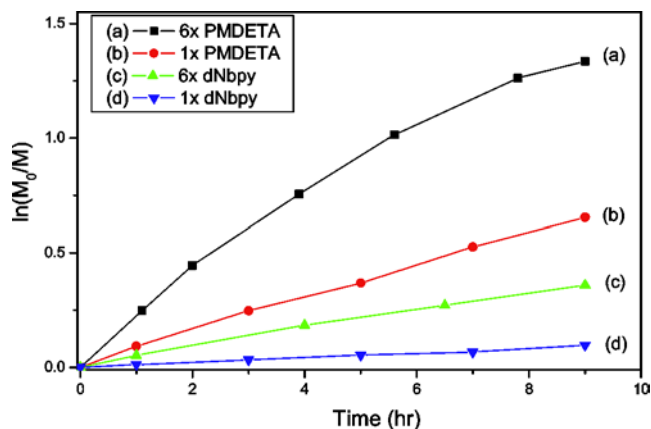


Figure 3. Semilogarithmic kinetic plot for the ATRP of 4VP with various amount of ligand at 80 °C [conditions: monomer (4 M), solvent: DMF, CuBr catalyst, PS macroinitiator $M_n = 8000$].

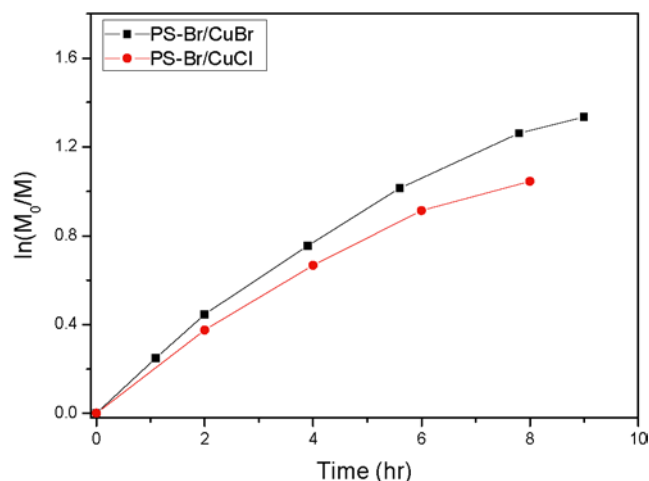


Figure 5. Semilogarithmic kinetic plot for the ATRP of 4VP with various amount of ligand at 80 °C by (●) with or (■) without halogen exchange [conditions: monomer (4 M); ligand: PMDETA; solvent: DMF, CuBr or CuCl catalyst, PS macroinitiator $M_n = 8000$].

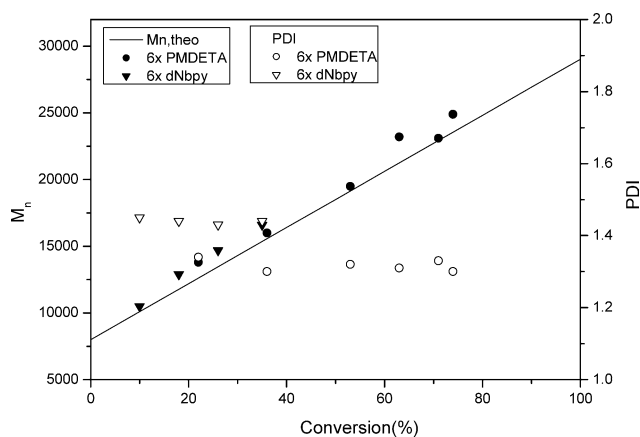


Figure 4. The dependence of the molecular weights and polydispersity of the block copolymers on monomer conversion under different reaction conditions. The linear line represents the theoretical M_n vs conversion.

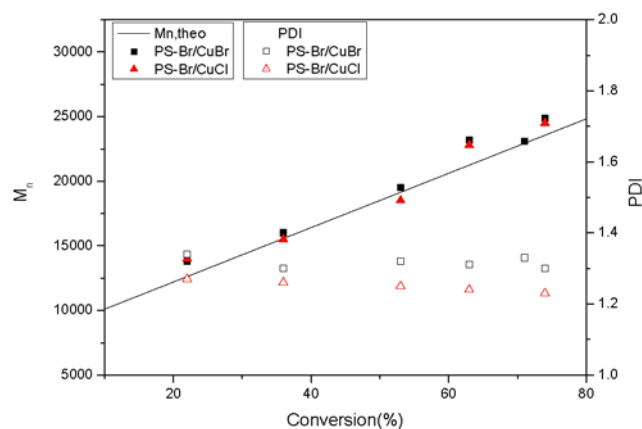


Figure 6. The dependence of the molecular weights and polydispersity of PS-b-P4VP copolymers on the monomer conversion with (●) and without (■) halogen exchange under different reaction conditions. [Conditions: same as in Figure 5.]

separated state. A large repulsion between the two different segments exists for the PS-*b*-P4VP system.

Thermal stability of block copolymers was examined by thermogravimetric analyzer (TGA) in the range of 30 to

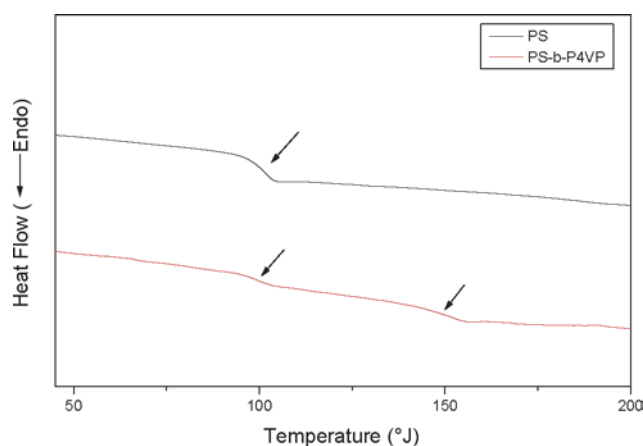


Figure 7. DSC thermograms of PS and PS-b-P4VP block copolymer.

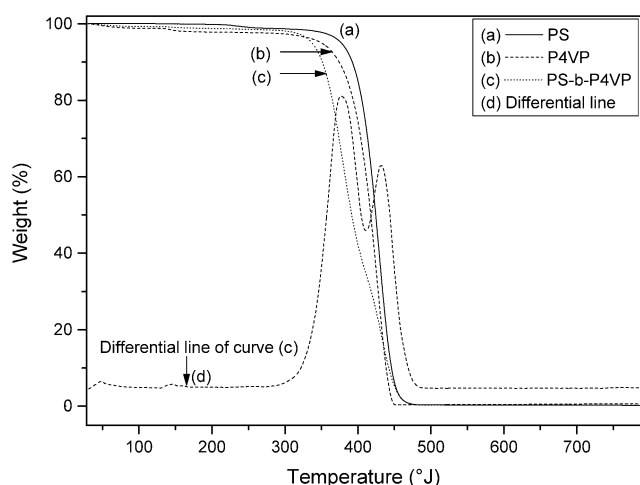


Figure 8. TGA thermograms of PS, P4VP and PS-b-P4VP block copolymer under N_2 atmosphere.

800 °C. As shown in Figure 8(c), TGA analysis of the block copolymer (sample 3, Table 1) shows a two-step thermal decomposition. In Figure 8(d), which was obtained by differentiating curve (c), we can observe two maximum points at 380 and 431 °C, respectively. The parent homopolymers have typically decomposed maximum points at 430 °C for PS ($M_n = 8000$) and 400 °C for P4VP ($M_n = 13000$) under nitrogen atmosphere, respectively. Therefore, the two maxima observed on the TGA trace for the PS-b-P4VP block copolymer can be assigned to the decomposition of the P4VP blocks at 380 °C and the PS blocks at higher temperature.

Conclusion

The formation of block copolymers of styrene and 4-vinylpyridine was investigated by using ATRP. We used of ATRP with commercial available ligands to syntheses well controlled block copolymers from styrene and 4-vinylpyridine monomers. MALDI-TOF-MS, 1H -NMR and GPC analyses verify that the successful synthesis of the PS-b-P4VP block copolymers. The kinetic study shows slower polymerization rate when using the CuBr/dNBipy catalyst system because the same pyridine unit functions as ligand and monomer. On

the contrary, faster polymerization rate is obtained by using the CuBr/PMDETA catalyst system. In the preparation of block copolymers starting from a PS macroinitiator, the use of halogen exchange technique results in better structural control for the polymerization of 4-vinylpyridine than that without the halogen exchange. DSC measurement of the PS-b-P4VP block copolymer exhibits two glass transitions, indicating that the resulting block copolymers are phase separated in condensed state. Two maximum differential peaks are found on the TGA trace for the PS-b-P4VP block copolymer as the result of the decomposition of the P4VP blocks at 380 °C and the PS blocks at higher temperature.

Acknowledgements

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